maximum height of the type used. The dots should be at least eight in number, six for the body of the letter, covering the whole height of such letters as *a* and *e*, and one dot each for the upper portion of such letters as *f* and *k*, and for the lower portion of such letters as *p* and *g*.

The note of each dot must be chosen so that it is easy to recognise its *omission* (not its *presence*, as in the case of the reading optophone previously described). Good results have been obtained with a set of notes with which both concords and discords can be obtained, according to the letters exposed. Such a series of notes is the following: g c′ d′ e′ g′ b′ c″ e″. But different arrangements may suit different ears.

A simple focussing device enables the operator to alter the length of the line of dots, and so adapt it to various sizes of type.

It is essential, in reading a line of type, that the alignment be perfect. This is ensured by a sliding device on the reading slab.

I wish to thank my lecture assistant, Mr. A. E. Vick, for his effective help in constructing the first working model of the instrument; and especially Sir Oliver Lodge for the kind interest he has taken in the whole investigation.

Studies of the Processes Operative in Solutions. XXIX.—*The Disturbance of the Equilibrium in Solutions by "Strong" and "Weak" Interfering Agents.*

By H. E. Armstrong, F.R.S., and E. E. Walker, B.Sc.

(Received May 7,—Read May 28, 1914.)

In a recent communication of this series (XXVI),* it was contended, that the change in the optical rotatory power of an aqueous solution of fructose which is produced by dissolving in the liquid a second substance, whether this be a salt or a non-electrolyte, is the consequence of an alteration in the proportion in which the two isodynamic forms of the compound are present in equilibrium. It was shown that substances such as the monhydric alcohols cause the change to take place in a direction opposite to that in which it takes place when substances such as sugar and salts are added: a similar antithesis has been observed in the course of these studies in numerous

* E. E. Walker, "The Disturbance of the Equilibrium in Solutions of Fructose by Salts and by Non-electrolytes," 'Roy. Soc. Proc.,' A, vol. 88, p. 246 (1913).

other cases in which the influence exerted by interfering agents has been determined.

To obtain sufficient data for the discussion of this problem, we have not only verified the results previously put forward, by repeating the observations and eliminating unsuspected sources of error, we have also measured the effect of a large number of substances other than those used previously.

In making up the solutions, air corrections were applied to all the weighings. The rotatory power of the solution of the fructose used was determined, in each experiment, before adding the interfering agent, as samples of the sugar varied in optical activity over a range of about 0·1 per cent. Two 400 mm. polarimeter tubes were used: the lengths of these had been compared by observing the rotations produced when both were filled with the same solution of cane sugar; the readings differed by less than 0·01 per cent. All measurements were made at 25° C. ±0·005, in mercury green light, with the polarimeter and apparatus described in No. XXII of these studies. The rotatory power was determined as soon as possible after adding the interfering agent, as the optical activity tends to increase gradually, especially in presence of the alcohols; usually the reading was taken 30–40 minutes after the temperature of the mixture was constant, in order to allow time for the completion of mutarotation, though in presence of large quantities of alcohol it was necessary to allow a longer interval to elapse, on account of the greatly reduced rate at which the change took place. The rotation produced by the optically active substances which were added was determined at about the same concentration as that at which they were to be used: in calculating the specific rotatory power of the fructose in their presence, the assumption was made that the rotatory power of the added substance was unchanged.

The densities were determined by means of density pipettes, the solution being drawn directly into these from the polarimeter tube immediately after the angular deviation had been observed. The quantity of interfering agent referred to is in all cases the amount associated with 100 grm. molecular proportions of hydrone (the fundamental molecule of water) and two molecular proportions of fructose, the volume of such a solution at 25° C. being 2030·1 c.c.

Throughout the account, the difference between this volume and the volume of the same solution after the addition of the specified amount of the interfering agent will be represented by ΔV. The significance of the other symbols that are used is as follows:—

M is the molecular proportion of interfering substance present per 100 molecular proportions of water;

$\Delta[\alpha]$ is the change in the specific rotatory power produced by the addition of M gramme-molecular proportions of the interfering substance;

n is the number of atoms of oxygen present in the interfering substance.

Table I.*

Interfering agent	No. of molecular proportions M	$\Delta[\alpha]$	$\Delta[\alpha]/M$	$\Delta V/M$
Cane-sugar	0·633	−1·67	−2·64	−212·6
Fructose	1·00	−0·89	−0·89	111·8
Methylglucoside (β)	1·221	−0·68	−0·56	137·2
Dulcitol	0·2485	−0·37	−1·49	120·3
Mannitol	0·765	−0·89	−1·16	120·3
Glycerol	1·373	−0·37	−0·27	71·8
Methanol	3·350	1·50	0·45	37·7
Ethanol	2·360	1·09	0·84	53·9
Propanol	1·805	2·13	1·18	69·7
Butanol (normal)	1·496	2·23	1·49	85·4
,, (secondary)	1·481	2·47	1·67	85·0
,, (tertiary)	1·430	2·21	1·54	86·0
,, (isoprimary)	1·482	2·24	1·51	85·4
Allylic alcohol	2·000	1·64	0·82	63·7
Acetone	1·607	1·71	1·06	66·2
Methylethylketone	1·278	1·86	1·45	81·7
Diethylketone	0·603	1·14	1·89	96·4
Methylal	1·897	1·90	0·97	79·6
Paraldehyde	0·771	1·15	1·49	122·7
Methylic acetate	1·706	1·95	1·14	72·0
Ethylic acetate	1·407	1·49	1·96	88·0
Benzylic alcohol	0·488	0·15	0·31	100·9
Phenol	1·327	−0·51	−0·38	86·5
Cresol	0·2775	−0·01	−0·04	103·0
Quinol	0·930	−1·31	−1·41	89·4
Pyrogallol	0·753	−1·31	−1·71	96·0
Salicin	0·2127	−0·44	−1·88	200·5
Acetonitrile	3·861	3·06	0·79	48·1
Propionitrile	2·833	3·39	1·19	64·1
Acetamide	2·615	0·41	0·16	55·8
Urea	2·690	−2·07	−0·78	44·9
Methylurea	1·981	−0·28	−0·14	62·4
Dimethylurea (symmetrical)	1·920	1·27	0·66	81·5
Diethylurea (unsymmetrical)	1·498	2·21	1·47	111·0
Glycine	2·000	−3·88	−1·59	45·5
Betaine	1·018	0·42	0·42	100·0
Asparagine	0·142	−0·32	−2·2	107·2
Thiourea	1·632	−1·81	−1·11	55·8
Salts:—				
Calcium chloride	1·054	−3·21	−3·04	28·3
Magnesium chloride	1·054	−2·13	−2·02	20·4
Ammonium ,,	2·110	−3·26	−1·55	36·75
Methylammonium chloride	2·000	−2·12	−1·06	55·35
Potassium chloride	1·556	−3·03	−1·95	31·0
,, bromide	2·000	−4·23	−2·10	36·7
,, iodide	1·968	−4·36	−2·22	48·2
Monopotassium phosphate	1·000	−2·73	−2·73	47·9
Disodium phosphate	1·000	−1·35	−1·35	6·0

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* Most of the values in this table are means of two experiments, in which very nearly equal quantities of interfering agent were used.

The results are recorded in Table I.* They serve broadly to justify the conclusions previously arrived at. As before shown, two classes of effects are produced. In the case of the monhydric alcohols and most weak solutes the change in rotatory power is positive: presumably such substances promote the formation of fructodextrose; not only sugars, polyhydric alcohols and salts generally (strong solutes) but also phenolic compounds and basic substances such as urea, thiourea and methylurea (though not the higher ureas) and the glycines† have the opposite effect on the rotatory power: they appear to promote the production of fructolævose. It is important to note that, whereas in all cases (except that of the two acetates) the effect becomes more positive as an homologous series is ascended, an accumulation of oxygen atoms involves a change in the opposite direction (compare propanol with glycerol, phenol with quinol and pyrogallol). It is also noteworthy that isomeric compounds usually produce results which differ but slightly. (Compare the butanols, dulcitol with mannitol, benzylic alcohol with cresol.) Nitrogen appears to have an effect similar to that of oxygen (compare acetonitrile and propionitrile with ethanol and propanol: acetamide with urea).

It is not an easy task to interpret the effect produced on fructose in an aqueous solution by various interfering agents, leading as these do presumably to an alteration in the proportions in which the two isodynamic forms are present in equilibrium, the change being sometimes in the one and sometimes in the other direction.

Since the previous communication on this subject was published, F. P. Worley has given an account of a most carefully conducted series of experiments with benzenesulphonic acid‡ (1 molecular proportion to 40 of hydrone) and the three sugars cane-sugar, glucose and fructose (one-quarter of a molecular proportion of each) in which the value of the specific rotatory

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* *The Effect of Various Substances on the Rotatory Power of Glucose in Solution.*—The results embodied in the following table, representing the effects produced on glucose, are of the same order as those obtained with fructose, though this sugar is much less sensitive than fructose.

Interfering agent	M	1/M Δ [α]
Methanol	6·68	0·14
Ethanol	4·67	0·20
Propanol	3·65	0·25
Butanol (tertiary)	2·83	0·32
Glycerol	3·65	0·17
Glycine	2·00	−0·15

† It would seem that such substances, though weak solutes, have a specific influence in virtue of their acid or basic character.

‡ These Studies, No. XXI, 'Roy. Soc. Proc.,' A, vol. 87, p. 555 (1912).

power of the sugar alone was determined and also that of the sugar in presence of the acid. The values obtained were:—

	Alone	With acid	Difference
Cane-sugar ...	78·28	77·19	1·09
Glucose	62·45	61·29	1·16
Fructose	−104·40	−108·56	4·16

In the case of cane-sugar, in which the possibility of an isodynamic form has not to be considered, as concentration has but little influence on the specific rotatory power, the alteration must be ascribed to the formation of a compound of the sugar with the acid which is of lower rotatory power than the sugar. Cane-sugar is composed of the more dextro-rotatory form of dextrose (the α-form) and of fructodextrose: both "radicles" doubtless combine with acid, though perhaps to a less extent than when they are free: presumably the amount of compound formed from a molecular proportion of cane-sugar would approximate to that formed from a molecular proportion of glucose together with the same quantity of fructodextrose.

The effects observed in the case of glucose and fructose—both of which are equilibrated mixtures—are doubtless the algebraic sum of the effects produced on their two isodynamic forms. Judging from Glover's observation that the specific rotatory power of α-methylglucoside is less affected than that of β-methylglucoside by salts, it is probable that the less dextrorotatory form of glucose (the β-form) and fructolævose both combine with acids and salts to a greater extent than the forms of more positive rotatory power: this greater tendency to combine would condition their formation in larger proportion in presence either of an acid or of a salt.

The high value deduced by Worley in the case of fructose appears to us to lend support to this view; from our own observations on the action of salts also we think that the increase in negative rotatory power of fructose is to be attributed mainly to the formation of an increased proportion of fructolævose rather than to the formation of a compound with the acid or salt of specially high negative rotatory power.

Further evidence that the greater affinity of fructolævose to metallic salts is probably the cause which determines the change of equilibrium was obtained from experiments resembling those with alcohol described in No. XXVI, p. 249. A solution of fructose having been heated to 25°, a weighed quantity of salt was introduced and dissolved as rapidly as possible, the liquid being warmed to compensate for the cooling but never above 25°: the solution was then introduced into the polarimeter tube. It was possible to make the first observation three minutes after adding the salt. A mean value of K was deduced by means of the equation

$$K = \frac{1}{t_2 - t_1} \log \frac{\alpha_\infty - \alpha_1}{\alpha_\infty - \alpha_2}.$$

To disturb the equilibrium of the solution, it was then heated to 80° and quickly cooled to 25°: the change in rotatory power was observed as before. In the case of the two salts used, the coefficient found was the same whichever way the change was caused to take place, as shown by the results recorded in Table II. It is therefore probable that in the case of fructose the addition of a salt changes the equilibrium between the two isodynamic forms but in a direction opposite to that caused by the addition of alcohol.

Table II.

Potassium chloride, 1·556 molecular proportions (see Table I)			Potassium bromide, 2·000 molecular proportions (see Table II)		
t	α	K	t	α	K
Mutarotation after displacement of equilibrium by addition of salt.					
	°			°	
0	—		0	—	
3	74·41		3	73·90	
6	·99	·101	5	74·40	·087
9	75·24	·084	7	·72	·083
12	·39	·092	10	75·01	·079
	·56		14	·23	·087
			19	·35	
				·41	
	Mean………	·092		Mean………	·084
Mutarotation after displacement of equilibrium by heat.					
$\frac{1}{4}$	72·39		0	68·06	
2	73·45	·096	3	71·37	·085
5	74·50	·091	6	73·17	·082
8	75·14	·111	9	74·22	·085
14	·50	·075	12	·79	·083
	·70		16	75·17	·078
			21	·39	·082
				·53	
	Mean………	·093		Mean………	·083

Table III.

	KCl	KBr
$\alpha_\infty - \alpha_0$	2·17	2·70
$\frac{1}{M}\Delta[\alpha]$ (calculated)	3·2	4·0
$\frac{1}{M}\Delta[\alpha]$ (observed)	3·03	4·21

If the total change $\alpha_\infty - \alpha_0$ be calculated from the equation

$$\frac{1}{t}\log\frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_1} = \mathrm{K},$$

α_0 rotation at time of time of mixing,
α_1 " " *t*, first observation,
α_∞ " " end point.

The values of $\Delta[\alpha]$ deduced from those of $\alpha_\infty - \alpha_0$ (Table III) approximate sufficiently to the observed values of $\Delta[\alpha]$ to indicate that the change is at least mainly due to the cause specified.

From the point of view advocated, the influence of fructose upon itself—that is to say the effect of concentration—is perhaps the most remarkable of all the cases studied: the fact that the negative rotatory power increases to a very marked extent as the concentration is increased cannot well be explained except as the consequence of an increase in the proportion of fructolævose. In the previous communication, it was contended that fructolævose forms a more stable hydrate than fructodextrose, the implication being that it was the more hydrated compound—if such be the case and it be formed in increasing amount as the solution is concentrated, it must be supposed that the formation of fructolævose is promoted by the tendency it has to combine with itself—to polymerise—much as it is by the presence of a salt with which it can combine.

This explanation is that already arrived at in the previous communication and we see no other way at present of explaining our results.

It appears logical to explain the action of all substances which increase the negative rotatory power of fructose in this way. Salts and cane-sugar and also other substances which have a negative effect doubtless exercise a dehydrating effect: this should promote the formation of fructodextrose, assuming that this form is the less hydrated; but if such be the case, the dehydrating tendency of the interfering agent is masked and overcome by the tendency it has to combine preferentially with fructolævose.

The substances which apparently promote the formation of fructodextrose, as they have a positive effect, do so, it may be supposed, because of the dehydrating effect they exercise—not directly by themselves combining with hydrone but in virtue of their power, as hormones, of dissociating the water complexes—thus rendering the water more greedy of hydrone (*cf.* Part VI)—and also the hydrated fructolævose molecules: such substances are to be credited with but slight power of combining either with the fructose molecules or with hydrone and they are far more active mechanically, by their interposition, than are the substances which promote the formation of fructolævose.

We may now consider the manner in which interfering agents generally produce the effects we have drawn attention to specially in the case of fructose.

Evaluation of the Effects Produced by Interfering Agents.

The problem is a very difficult one, on account of its complexity, as the effects considered cannot well be otherwise than the outcome of a variety of adjustments: though we are fully conscious that the solution offered can only be regarded as a first approximation, we venture to put it forward for consideration, to provoke further discussion of the issues, as these appear to be of consequence especially in connexion with physiological phenomena.*

The one class of interfering agents includes all those neutral, soluble substances which can be classed broadly as *hormones*—substances which diffuse more or less readily through a differential septum such as that with which the barley grain is provided and also promote diffusion of water into the grain: the other class includes both the strong electrolytes and substances such as the sugars, in fact *anhormones* generally—*i.e.* materials which do not diffuse through the differential septum of the barley grain. It would seem to be probable that the special activity of the one class of substances (the hormones) is to be connected with their mobility in solution: that of the other class (the anhormones) with their relative immobility.

The difference is not merely that which prevails between electrolytes and non-electrolytes, as sugar and salts produce like effects and as many weak electrolytes are to be ranged with the hormones. Apparently, a wider generalisation is possible, inasmuch as the one class includes all substances having a strong affinity with hydrone—the fundamental molecule of water—with which substances of the other class—the hormones—have but slight tendency to associate. As the strong acids and strong bases are among the former, these—the anhormones—may be conveniently spoken of as "*strong solutes*": whilst the other class—the hormones—may be termed *weak solutes.* It is scarcely necessary to point out that the strong shade insensibly into the weak, in fact, that no hard and fast line of demarcation is possible.

It is obviously important to arrive at an understanding of the manner in which the two classes of substance affect the equilibrium in a solution and to explain the fact that, in some way, they produce opposite effects; this is particularly desirable in view of the special physiological activity of hormones.

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* *Cf.* H. E. Armstrong, "The Properties of Alcohol in relation to its Physiological Effects," 'Journ. Inst. Brewing,' vol. 19, p. 518 (1913).

Throughout these communications, exception has been taken to the practice of using solutions made up to a particular *volume* (volume-normal solutions) instead of using solutions in which the amount of solvent is maintained constant (weight-normal solutions). In the former case, no constant ratio is maintained between the mass of the solvent and that of the solute, the quantity of the former varying in amount according to the extent to which it is displaced by the solution: in the latter, the only variable introduced consciously is the amount of substance dissolved per unit of solvent: and in cases in which the action of an interfering agent is studied, the amount of the interfering agent is alone varied, that of the solvent and solute being kept constant.

In the case of extremely dilute solutions, the two methods yield similar results within the limits of experimental error, as the mass of the solvent is practically proportional to the volume of the solution. In the case of concentrated solutions, however, alteration of the amount of solute in a given volume of solution is accompanied by a more or less considerable alteration of the amount of solvent in a given volume, so that there are at least two variables. As it is desired to study the effect of the solute on the solvent and *vice versâ*, it is essential that the proportions in which these are present be known: therefore weight-normal solutions must be used. When this method is adopted, however, the volume of the solution varies as the proportions by weight of the constituents are altered, so that some part of the change observed may well be due to the variation in the volume distribution of the interacting substances.

The question arises whether it be not possible, in some way, to make allowance for alteration in volume and more generally to take into account the purely mechanical, screening action which substances have apart from the influence they exercise through their affinities: this we have endeavoured to answer in the present communication.

Taking into account the effect of alcohols and other substances on—

(1) the rate at which cane sugar is hydrolysed;
(2) the conductivity of electrolytes;
(3) the solubility of salts in water;
(4) the rate at which water enters into the barley grain;
(5) the rate at which Urea is formed from Ammonic cyanate;

it will be admitted, probably, that weak solutes (hormones) act mainly in virtue of the dissociating effect which they exercise mechanically within the system into which they are introduced. It might reasonably be expected that this mechanical effect would be proportional to the change in volume produced by the addition of the interfering agents.

In the present communication, an attempt is made to separate the effect of an added substance into two independent components.

(1) a purely mechanical, diluent or screening effect which causes *dissociation* of the water complexes, of the complex molecules of the solute and of the hydrates of the solute;

(2) an influence, opposite in effect to the first, proportional to the attractive powers or residual affinities of the admixed substances, promoting *association* in various ways.

Table IV.

Interfering substance.	Diagram 1 $\frac{10nM}{\Delta V}$	Diagram 2 $\frac{M(10n+3n')}{\Delta V}$	$\frac{\Delta[\alpha]}{\Delta V}$
1. Cane-sugar	0·517	0·686	−0·0124
2. Fructose	0·537	0·698	−0·0080
3. Methylglucoside (β)	0·438	0·590	−0·0041
4. Dulcitol	0·499	0·648	−0·0124
5. Mannitol	0·499	0·649	−0·0097
6. Glycerol	0·418	0·543	−0·0038
7. Methanol	0·266	0·345	0·0119
8. Ethanol	0·186	0·297	0·0156
9. Propanol	0·144	0·273	0·0169
10. Butanol (normal)	0·117	0·258	0·0175
11. „ (secondary)	0·118	0·259	0·0197
12. „ (tertiary)	0·116	0·256	0·0179
13. „ (isoprimary)	0·117	0·258	0·0177
14. Acetone	0·151	0·287	0·0160
15. Methylethylketone	0·122	0·269	0·0178
16. Diethylketone	0·104	0·259	0·0196
17. Methylal	0·252	0·364	0·0122
18. Paraldehyde	0·245	0·392	0·0121
19. Ethylic acetate	0·227	0·364	0·0120
20. Water	0·555	0·555	—

Data for Diagrams 1 and 2.

On the assumption that the mechanical effect of the interfering substance is a simple diluent action, proportional to the increase in volume which it occasions, the attempt may be made to evaluate the two effects by comparing the changes in rotatory power caused by the quantities of the interfering agents which produce like changes in volume.

If, within the narrow range covered by the experiments, the change in rotatory power produced by the interfering agent* be proportional to the amount added, the value sought is given by the expression

$$\frac{\Delta[\alpha]}{\Delta V},$$

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* When the results quoted in No. XXVII (p. 393) of these studies are plotted, it is obvious that in the case of alcohol no great error is introduced by this assumption, so

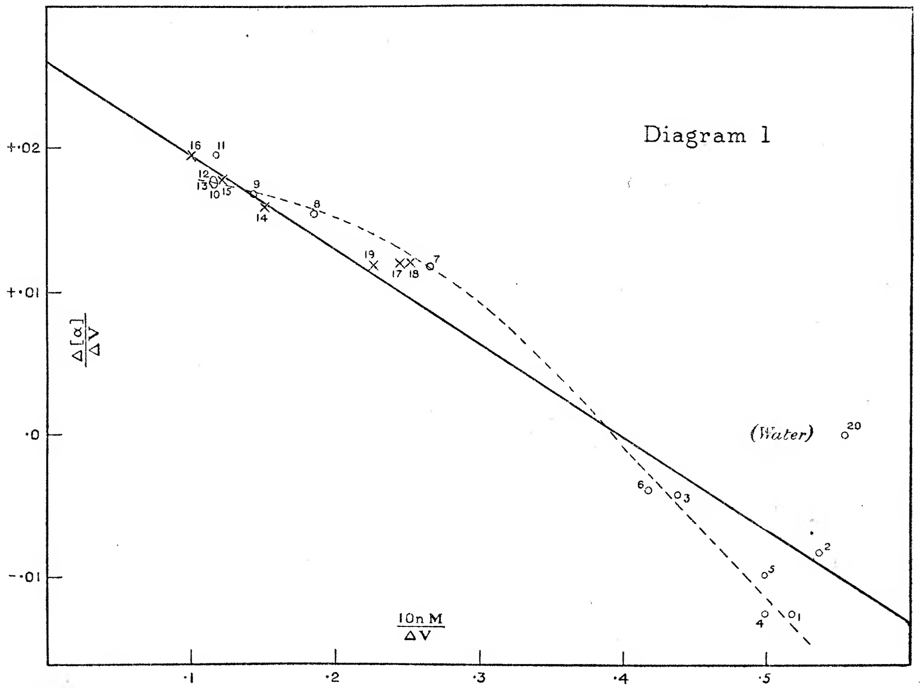
Diagram 1
+·02
+·01
·0
−·01
Δ[α]/ΔV
10n M/ΔV
·1
·2
·3
·4
·5
(Water)
16
11
12
13
10
15
9
14
8
19
17
18
7
20
6
3
2
5
4
1

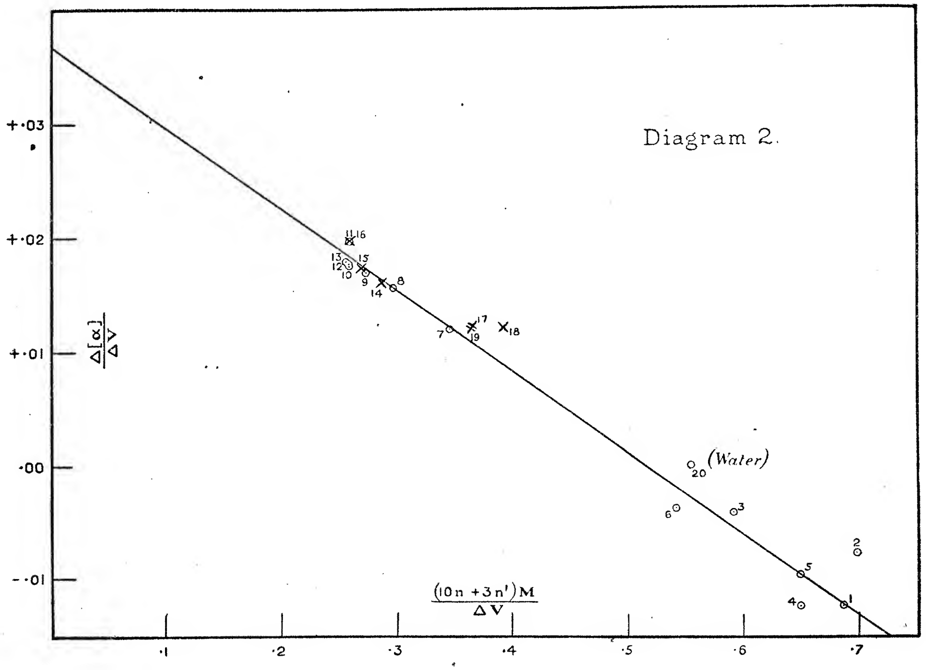
Diagram 2.
+·03
+·02
+·01
·00
−·01
Δ[α]/ΔV
(10n +3n′)M/ΔV
·1
·2
·3
·4
·5
·6
·7
(Water)
11
16
13
12
10
15
9
14
8
7
17
19
18
20
6
3
2
5
4
1

the change of rotatory power produced by the quantity of substance which causes an increase in volume of 1 c.c. in a solution of 2 gramme-molecular proportions of fructose in 100 of hydrone.

In Diagram 1 this quantity is plotted against the number of grammes of oxygen in the quantity of interfering agent used $n\mathrm{M}/\Delta\mathrm{V}$ (see Table IV). Though the various points are not strictly in line, nevertheless, a very general relationship between the effect produced by a paraffinoid oxygen compound and the number of oxygen atoms it contains is obvious. A straight line drawn between the points cuts the rotation axis at about $+0{\cdot}026$; this value may be taken as a first approximate expression of the effect which would be produced by 1 c.c. (apparent) of a substance free from oxygen.

A closer study of the diagram reveals the fact that all substances (*i.e.* paraffinoid alcohols and sugars) lie on a curve (the dotted line) rather than on a straight line. This may mean: either that the activity of the oxygen varies as the amount present is increased—or that the hydrocarbon radicle itself has a chemical activity which cannot be neglected—or still more probably that both of these causes are at work. It is, however, interesting to note that the curvature can be eliminated if the assumption be made that the methylene group has an influence just about one-third as great as that of the oxygen atom.

If the ordinates are calculated from the expression

$$\frac{\mathrm{M}(10n+3n')}{\Delta\mathrm{V}},$$

in which n' is the number of carbon atoms in the molecule, Diagram 2 is obtained. The points in this diagram lie very near to a straight line and the value of the hypothetical substance having no residual affinity is raised to 0·037. It is to be noticed that water, which may be regarded as the lowest alcohol, now comes into line with the polyhydric alcohols; this is an important argument in favour of the view that carbon is in part responsible for the effect produced, as it is only when this is taken into account that water is brought into line with the compounds containing carbon.

Using the value 0·026 arrived at in Diagram 1 as the "volume-coefficient," the change in rotatory powers per gramme molecular proportion of substance added, viz. $\Delta[\alpha]/\mathrm{M}$ is equal to $0{\cdot}026\,\Delta\mathrm{V}/\mathrm{M}-\mathrm{A}$, in which A is the residual affinity or chemical effect per gramme molecular proportion: whence it follows that

$$\mathrm{A} = 0{\cdot}026\Delta\mathrm{V}/\mathrm{M}-\Delta[\alpha]/\mathrm{M}.$$

---

long as the change in rotatory power does not exceed 3° or 4°, a quantity not exceeded in the observations we are discussing (*cf.* Wenden, 'Biochem. Zeit.,' vol. 30, p. 357).

By substituting 0·037, the value of the volume-coefficient arrived at in Diagram 2, other values of A are obtained: but since these are obtained on the assumption that carbon has a value equal to about one-third that of an oxygen atom, this value must first be subtracted before the variation of A can be correlated with the number of oxygen atoms in the molecule

$$A = A' + 0{\cdot}23n' = \frac{1}{M}(0{\cdot}037\Delta V - \Delta[\alpha]).$$

The coefficient 0·23 is chosen by trial, approximately one-third the mean value of A'/n.

Influence of Oxygen Compounds.

In Table V are given the values of A found in the case of a series of paraffinoid oxygen compounds. It will be noticed that these values differ considerably in the case of different compounds: on dividing them, however, by the number of oxygen atoms in the molecule, approximately constant values (column 5) are obtained: in other words, the chemical effect is approximately proportional to the number of atoms of oxygen in the molecule. Though only another way of expressing the result arrived at by means of Diagram 1, this has the advantage that it is applicable to substances containing radicles other than oxygen. The two compounds in which the departure is greatest are allylic alcohol and methylic acetate, the value in

Table V.

Interfering substance	$\frac{0{\cdot}026\Delta V}{M}$	$\frac{\Delta[\alpha]}{M}$	A	$\frac{1}{n}A$	$\frac{1}{n}A'$
Cane-sugar	5 ·53	−2 ·64	8 ·17	0 ·74	0 ·71
β-Methylglucoside	3 ·57	−0 ·56	4 ·13	0 ·69	0 ·67
Fructose	2 ·81	−0 ·89	3 ·70	0 ·62	0 ·61
Dulcitol	3 ·13	−1 ·49	4 ·62	0 ·77	0 ·76
Mannitol	3 ·13	−1 ·16	4 ·29	0 ·72	0 ·70
Glycerol	1 ·87	−0 ·27	2 ·14	0 ·71	0 ·74
Methanol	0 ·98	0 ·49	0 ·53	0 ·53	0 ·72
Ethanol	1 ·40	0 ·84	0 ·56	0 ·56	0 ·70
Propanol	1 ·81	1 ·18	0 ·63	0 ·63	0 ·71
Butanol (normal)	2 ·22	1 ·49	0 ·73	0 ·73	0 ·75
„ (secondary)	2 ·21	1 ·67	0 ·54	0 ·54	0 ·56
„ (tertiary)	2 ·24	1 ·54	0 ·70	0 ·70	0 ·74
„ (isoprimary)	2 ·22	1 ·51	0 ·71	0 ·71	0 ·73
Allylic alcohol	1 ·66	0 ·82	0 ·84	(0 ·84)	(0 ·85)
Acetone	1 ·72	1 ·06	0 ·66	0 ·66	0 ·70
Methylethylketone	2 ·12	1 ·45	0 ·67	0 ·67	0 ·65
Diethylketone	2 ·51	1 ·89	0 ·62	0 ·62	0 ·53
Methylal	2 ·07	0 ·97	1 ·10	0 ·55	0 ·64
Paraldehyde	3 ·19	1 ·49	1 ·70	0 ·57	0 ·53
Methylic acetate	1 ·87	1 ·14	0 ·73	0 ·37	0 ·42
Ethylic acetate	2 ·29	1 ·06	1 ·23	0 ·61	0 ·64
Water	0 ·47	—	0 ·47	(0 ·47)	0 ·66

the former case being high and in the latter low: that of the acetate is the more remarkable departure, as the ethylic salt affords a "normal" value. The high value given by allylic alcohol is undoubtedly to be connected with its ethenoid structure.

The values obtained on using the more complex hypothesis, viz., that the carbon has an effect equal to about one-third that of the oxygen atom, are given in Column 6, A′ being the value arrived at by making allowance for the number of carbon atoms present. The values deduced for alcohols, on this hypothesis, are more nearly alike, most of them lying between about 0·70 and 0·75.

Table VI contains the values of A deduced in the case of several benzoid compounds. The apparent influence of the benzene radicle is evaluated by subtracting 0·65 *n*, the mean value of an oxygen atom (Table V) for each oxygen atom present in the molecule. It is obvious that the phenyl group has a very special influence, either directly or indirectly.

Table VI.—Values of A for Benzenoid Compounds showing the Influence of the Benzene Complex.

Interfering agent	$\frac{0 \cdot 026 \Delta V}{M}$	$\frac{\Delta[\alpha]}{\Delta V}$	A	*n*	A−0·65*n*
Benzylic alcohol	2·62	0·31	2·31	1	1·7
Phenol	2·25	−0·38	2·63	1	2·0
Cresol	2·68	−0·04	2·72	1	2·1
Quinol............................	2·32	−1·41	3·73	2	2·4
Pyrogallol	2·50	−1·74	4·24	3	2·3
Salicin	5·24	−2·06	7·30	7	2·8*

* If 0·69, the mean value of *A*/*n* in sugars and hexahydric alcohols, be used, the value for the benzene radicle in column 5 is reduced to 2·2 and so made more nearly compatible with the others.

In dealing with the nitrogen compounds and certain benzene derivatives the second hypothesis will not be taken into account.

Influence of Nitrogen Compounds.

The values of A deduced for a series of nitrogen compounds (Table VII) are of interest as showing that, as observed in the case of other properties, the effect* of this element is far less "constant" than that of oxygen. The effect of the nitrogen in the two nitriles is about the same; urea has about the same value as acetamide, which presumably contains nitrogen in the same form of combination. The values of the substituted ureas, on the other hand, are lower, methylurea being lower than urea and dimethylurea still lower. In glycine, betaine and asparagine, either nitrogen or oxygen must have abnormally high values: it is noteworthy that, just as the value of A in urea is reduced by the substitution of the amido hydrogen by methyl, so is the corresponding value of glycine reduced by the substitution of the atoms of hydrogen attached to nitrogen; it is reduced by a little more than the difference between urea and unsymmetrical diethylurea. Obviously these differences invite further enquiry.

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* The apparent effect of the nitrogen atom is obtained by subtracting 0·65*n* from A and dividing by *n*″, the number of nitrogen atoms in the molecule. See last column, Table VIII.

Table VII.

Interfering substance.	$\frac{0{\cdot}026\Delta V}{M}$	$\frac{\Delta[\alpha]}{M}$	A	Value of oxygen (assumed).	n''	$\frac{A - 0{\cdot}65n}{n''}$
Acetonitrile	1·25	0·79	0·46		1	0·46
Propionitrile	1·66	1·19	0·47		1	0·47
Acetamide	1·45	0·16	1·29	0·65	1	0·64
Urea	1·17	−0·78	1·95	0·65	2	0·65
Methylurea	1·62	−0·14	1·76	0·65	2	
Dimethylurea (symmetric)	2·12	0·66	1·46	0·65	2	0·41
Diethylurea (asymmetric)	2·89	1·47	1·42	0·65	2	
Glycine	1·18	−1·59	2·77	1·3	1	1·47
Betaine	2·60	0·42	2·18	1·3	1	0·88
Asparagine	2·79	−2·2	5·0	1·05	2	1·5
Thiourea	1·45	−1·11	2·50		2	

Influence of Salts.

The results obtained with a number of haloids and with the two phosphates are given in Table VIII. The marked difference between the values of A in

Table VIII.—Values of A calculated for various Inorganic Salts.

Interfering agent	$\cdot026\Delta V/M$	$\frac{\Delta[\alpha]}{M}$	A
Magnesium chloride	0·53	−2·02	2·55
Calcium chloride	0·74	−3·04	3·78
Ammonium chloride	0·96	−1·55	2·51
Methylammonium chloride	1·44	−1·06	2·50
Potassium chloride	0·81	−1·95	2·76
„ bromide	0·95	−2·10	3·05
„ iodide	1·25	−2·22	3·47
Disodium phosphate	0·16	−1·35	1·51
Monopotassium phosphate	1·24	−2·73	3·97

the case of the three potassium salts is in accordance with the view generally held that the residual affinity of salts depends chiefly on the acid radicle, though this is influenced by the metal, as shown by the difference between magnesium and calcium chlorides. The considerable differences between ammonium and methylammonium chloride in the values of $\Delta [\alpha]/M$ and the close similarity of the values of A are indications that the difference is chiefly due to the volume effect of the methyl group.

Precipitation of Salts.

It now remains to be seen how far the conception of the existence of two opposing forces can be used to explain other effects of dissolved substances on solutions.

Table IX.—Values of A and A/*n* calculated from the Effect of various Substances on the Solubility of Potassium Chloride in Water.

Interfering agent.	M	$10 \log_e \frac{S_2}{S_1}$	ΔV	10 A	*n*	10A/*n*
Glucose	1·00	0·365	121·1	3·99	6	0·66
Mannitol	0·215	0·008	26·8	3·79	6	0·63
Glycerol	0·25	−0·027	17·6	1·94	3	0·65
Glycol	1·00	−0·237	51·1	1·29	2	0·65
Methanol	3·00	−1·164	93·9	0·55	1	0·55
Ethanol	2·00	−1·309	88·6	0·67	1	0·67
Propanol	1·00	−0·965	54·5	0·67	1	0·67
Paraldehyde	0·0833	−0·127	8·7	1·6	3	0·53

S_1 = solubility of potassium chloride.
S_2 = solubility of potassium chloride in presence of interfering agent.

The equilibrium between a solid salt and its aqueous solution may appear to be very different from that of two isodynamic forms of fructose: nevertheless there are points of similarity in the problem. The equilibrium in a saturated solution may be represented thus:—

$$\text{Salt } (H_2O)_x \rightleftarrows \text{Salt} + x H_2O,$$

a process which has something in common with the conversion of fructose into a less hydrated form. The case is complicated, however, by the fact that the quantity of salt in solution varies at the same time as that of the added substance. The extent of the influence due to this variation is not known: the assumption may be made, however, that its magnitude is proportional to the change in concentration so long as this is small. We may therefore write—

$$A = \frac{1}{M}(C\Delta V + \Delta S + C'\Delta S),$$

in which ΔS is the increase or decrease in solubility, C' a constant depending on the magnitude and sign of the influence referred to above.

It is obvious that the quantity C' affects C and A to the same extent and will not interfere with the relationship between them—

$$\frac{A}{1+C'} = \frac{1}{M}\left(\frac{C}{1+C'}\Delta V + \Delta S\right) \quad \text{or} \quad A'' = \frac{1}{M}(C''\Delta V + \Delta S),$$

and therefore need not be expected to have a very great influence.

ΔS can only be used for very small percentage changes in solubility. Rothmund has shown* that the influence of a substance on solubility is approximately proportional to the logarithmic function, $\log \frac{S_2}{S_1}$; this has been used in calculating the values of A given in Table IX from data supplied by Armstrong and Eyre.† The value 0·030 deduced graphically has been assigned to C and values of A calculated according to the equation:

$$A = \frac{1}{M}\left(0{\cdot}0031\,\Delta V + \log_e \frac{S_2}{S_1}\right).$$

The values show that a general relationship exists between the values of A and the number of oxygen atoms in the molecule.

The Hydrolysis of Cane-sugar.

Whilst neutral salts increase the rate at which cane-sugar is hydrolysed, alcohols, as Caldwell and Worley have shown, have the opposite effect. In such a case, as changes may take place in the catalyst as well as in the substance which is changing, the velocity at which a chemical change takes place is subject to the action of a number of factors in excess of those by which a change in the equilibrium of two isodynamic substances is influenced: nevertheless, it is clear from Caldwell's values that the influence exercised by lactose, glucose, glycerol and ethylic alcohol is of the same order as that which these substances exercise on the solubility of salts and on the equilibrium of the two forms of fructose.

The chief difficulty that arises in attempting to evaluate their influence is to decide on a method of expressing the increase or decrease in the rate of hydrolysis when this is a large percentage of the whole change: in default of further knowledge, the following expression has been used:—

$$A = \frac{1}{M}\left(0{\cdot}0021\,\Delta V - \frac{K_2 - K_1}{K_2}\right).$$

K_1 = Velocity coefficient in absence of interfering agent,
K_2 = " " in presence of "

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* 'Zeit. Phys. Chem.,' vol. 69, p. 523.

† 'Proc. Roy. Soc.,' A, vol. 79, p. 566; vol. 84, p. 123.

This has been applied to the data given by Caldwell. The results, though few in number, tend to show that the two opposing forces contemplated are at work governing the rate at which the chemical action takes place. Values of A, giving C the value 0·021, are shown in Table X.

Table X.—Values of A of various Substances calculated from their Effect upon the Rate at which Cane-sugar is Hydrolysed by Chlorhydric Acid.

Interfering agent	M	ΔV	$0{\cdot}021\,\Delta V$	$10\,\frac{K_2-K_1}{K_2}$	10A	n	$10A/n$
Lactose	½	110·6	2·32	0·09	4·64	11	·42
Glucose	1	120·2	2·53	0·16	2·68	6	·45
”	½	57·1	1·20	0·09	2·58	6	·43
Glycerol	1	75·8	−1·59	−0·49	1·10	3	·37
Alcohol	1	59·8	1·26	−0·84	0·42	1	·42
$(NH_4)Cl$	1	44·4	0·93	3·06	3·99		
KCl	1	31·6	0·66	3·27	3·93		
NaCl	1	18·8	0·39	4·47	4·86		
$BaCl_2$	1	33·6	0·70	9·28	9·98		

Velocity of Chemical Action in Various Solvents.—Patterson and Montgomerie* have collected a number of cases in which the velocity of chemical action has been compared in different solvents. On account of the regularity of the order in which solvents are active in various cases, it is at least probable that their residual affinity plays an important part.

Values of $AM/\Delta V$, reduced to that of methylic alcohol as unity, are given in the first column of Table XI.

Table XI.

Solvent.	$A\,\frac{M}{\Delta V}$	Menchutkin.	Patterson and Montgomerie.
Methanol	1·00	1·00	1·00
Ethanol	0·74	0·71	0·90
Propanol	0·64	—	0·82
Butanol	0·59	0·50	0·46
Allylic alcohol	0·95	0·84	0·75
Benzylic alcohol	1·64	2·59	1·52

This quantity is practically the "amount" of residual affinity per cubic centimetre. The values in columns 2 and 3 are the velocity coefficients reduced to that of methylic alcohol, in the case (A) of the interaction of triethylamine and ethyl iodide (Menchutkin); (B) of the transformation of syn-anisaldoxime into anti-anisaldoxime (Patterson and Montgomerie).

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* 'Trans. Chem. Soc.,' vol. 101, p. 34 (1912).

The similarity between Menchutkin's values and those in the first column is striking: Patterson and Montgomerie's values are not so closely in agreement with those calculated, though the order, excepting in the case of allylic alcohol, comes out the same.

Taking into account the results arrived at by applying our method to a variety of interactions very different in character, in view of the broad agreement with the hypothesis considered, we venture to think that it has been justified and that the discussion will serve to overcome the reluctance with which weight-normal solutions are used.

Senter, in a recent reference to certain communications of this series of studies, criticises the use of such solutions : while admitting that the method has considerable advantages, he states that it has one serious disadvantage *from the point of view of the kinetic theory.* Taking the case of the hydrolysis of cane-sugar as an example, he asserts that the mean free path of the interacting molecules depends on the total volume and that, other things being equal, the velocity of interaction must depend therefore on the total volume.

We have difficulty in understanding this argument and its application to our work. If it be desired to study the effect of a third substance C on the interaction of A and B in solution in some liquid, without varying the proportions of A and B to the solvent, so that there may be only one variable, no other method is possible than that of merely adding the desired amount of C. C then exercises a certain screening effect and would equally exercise the effect whether the solution were made up to a definite volume or by weight. Our desire in this communication has been to contrast the effect produced by the substance as a mere screen with that which it exercises in other ways, so that we might be in a position to form an estimate of the "chemical" effects produced by various substances.

The results obtained by means of the method appear to justify the conclusion that in the case of the homologous alcohols, for example, when allowance is made for the screening effect they exercise, their molecular chemical activity varies but slightly throughout the series; moreover, that the activity per atom of oxygen in related paraffinoid compounds is practically the same. It seems to us, therefore, that we have devised a method of treatment by means of which many diverse phenomena manifest in solutions may be correlated.